

SCIENCE FOR CERAMIC PRODUCTION

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TECHNICAL CERAMIC BASED ON MIXTURES OF POTASSIUM POLYTITANATE AND TITANIUM OXIDE

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The regularities of the interaction of amorphous potassium polytitanate with titanium oxide during calcination of their mixtures, taken in different proportions, are studied. The mechanism and sequence of phase transformations in the experimental mixture are analyzed. It is found that the introduction of titanium oxide into potassium polytitanate results in the formation of a denser ceramic structure, consisting of compacted nanofibers of potassium hexatitanate, stabilized by TiO₂ crystals.

Key words: potassium titanate, nanopowders, ceramic, structure, mechanical strength.

Potassium titanate crystals with $n = 6 - 8$ have a tunnel fiber structure and are characterized by high strength and heat-insulation properties as well as high chemical stability and electric resistance and a low coefficient of friction [1, 2]. On the other hand the structure of potassium titanate nanofibers (whiskers) is similar to that of asbestos, which the ILO (International Labor Organization) and other international and national organizations classify as extremely dangerous, carcinogenic, dust-forming fibers. In addition, in order to form green compacts based on powders consisting of fibrous particles it is necessary to use extremely high pressure and expensive equipment; this eliminates their use for the production of potentially promising high-strength ceramic materials [3].

These problems stimulated the development of amorphous (weakly crystalline) potassium titanates, called potassium polytitanates [4]. The stoichiometry (molar ratio TiO₂/K₂O) of this form of the compounds varies over a wide range and the particles possess a safe, flaky form. Such precursor materials are not dangerous for the health of technical workers during production and subsequent use. However, during subsequent heat treatment potassium polytitanates can form fibrous structures of crystalline potassium polytitanates [4, 5]. For example, in [5] ceramic samples with bending strength to 800 MPa were synthesized during

sintering of green parts obtained on the basis of potassium polytitanate with molar ratio TiO₂/K₂O = 6.

However, it should be kept in mind that the main drawback of potassium polytitanates is the complexity of obtaining precursor materials with a prescribed ratio TiO₂/K₂O (preferably close to 6), because as this ratio increases the cost of the product increases significantly since its yield during synthesis decreases. At the same time, on heating, potassium polytitanates with relatively low ratio TiO₂/K₂O (3.5 – 4.5) crystallize with formation of a low-strength ceramic consisting of weakly bound crystals of potassium tetratitanate or their mixtures with potassium hexatitanate. Since the mechanical strength of potassium tetratitanate is significantly lower than that of potassium hexatitanate, the question of how to solve this problem arises.

In the present work we investigate the possibility of obtaining high-strength ceramic using raw mixtures containing potassium polytitanate powders with relatively low titanium oxide content (molar ratio TiO₂/K₂O = 4.2) and a powder of titanium oxide itself, which as a raw component fills the deficiency of TiO₂ in the system and makes it possible to increase the molar ratio TiO₂/K₂O to 6.

Potassium titanate was synthesized by the procedure published in [4]. Titanium oxide powder (chemically pure grade anatase) with average particle size 5 μm underwent treatment in melt containing 10 wt.% KOH and 90 wt.% KNO₃ and obtained from chemically pure grade reagents. The content (by weight) of TiO₂ and salt melt in the system

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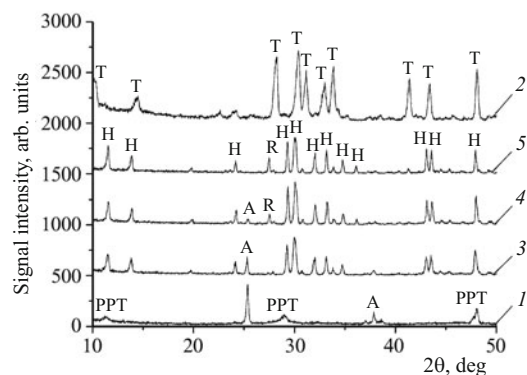


Fig. 1. X-ray diffraction patterns of the initial potassium polytitanate (1), ceramic obtained on its basis (2) and ceramic obtained on the basis of the following mixtures (composition in molar fractions, %): PPT(100) + TiO₂(40) (3); PPT(100) + TiO₂(50) (4) and PPT(100) + TiO₂(60) (5); A) TiO₂ (anatase); R) TiO₂ (rutile); H) potassium hexatitanate K₂Ti₆O₁₃; T) potassium tetratitanate K₇Ti₄O₉.

was maintained in the ratio 1 : 10. Synthesis was performed at 500°C over 2 h in an alundum crucible using a Thermo-Line-2300 electric muffle furnace. At the completion of heat-treatment the contents of the crucible were poured into distilled water, and the product obtained was washed and filtered using No. 42 filtering paper.

The potassium polytitanate (PPT) filtered in this manner comprised an amorphous powder, consisting of flakes, whose chemical composition, according to local x-ray microanalysis (SEM EDS-S60 DX90 attachment to a Jeol-5800LV scanning electron microscope) is determined by the formula $K_2O \cdot 4.7TiO_2$. Since potassium titanate at temperatures above 800°C can enter into chemical interaction with titanium oxide [5], the amount of TiO_2 additionally added to the system was calculated on the basis of obtaining molar ratio $TiO_2/K_2O \geq 6$ in the system. It can be supposed that on heat-treatment a system with general stoichiometry corresponding to potassium hexatitanate will crystallize owing to the interaction of amorphous PPT with additionally added TiO_2 and high-strength fibrous $K_2Ti_6O_{13}$ crystals will be formed. If the ratio TiO_2/K_2O in the system will not exceed 6, then the excess titanium oxide which has not entered into reaction with PPT with $K_2Ti_6O_{13}$ being formed will play the role of a component of the ceramic composite impeding

excessive growth of $\text{K}_2\text{Ti}_6\text{O}_{13}$ crystals, which will result in a ceramic with looser structure and lower mechanical strength [6].

In this connection samples with the content (by weight) of the additionally ($> 100\%$) added titanium oxide ranging from 20 to 60%, corresponding to molar ratio $\text{TiO}_2/\text{K}_2\text{O}$ in the reactive system from 5.3 to 7.4, were prepared.

The mixtures of the raw materials were homogenized in a porcelain ball mill and pressed in a stainless steel die, using a hydraulic press, into rectangular samples with the dimensions $25.0 \times 12.5 \times 6.0$ mm. Next, the samples were heat-treated by heating at the rate 10 K/min to 1100°C, soaked at this temperature for 1 h and then cooled at the rate 10 K/min to room temperature.

The microstructure of the ceramic materials obtained was studied with a Jeol-5800LV scanning electron microscope. A DRON-4 diffractometer was used to study the phase composition of the ceramic.

The mechanical strength of the ceramic in compression (according to GOST 6462–85) was determined using cubic samples (cube edges 40 ± 2 mm). The average strength was calculated from the measurements for eight samples. The microhardness was determined with a PMT-3 microhardness meter, and the resistance to thermal shock was determined according to GOST 473.5–81. The friction coefficient of the ceramic was calculated with the aid of an II-2 universal friction machine, which for measuring torsion provided uniform rotation of cylindrical samples of the ceramic (12.5 mm in diameter) under a 30 N load on the surface of a stainless steel plate with linear rotational speed 50 m/sec.

The x-ray diffraction patterns of the initial PPT powder as well as the ceramic obtained on its basis and on the basis of its mixtures (100% PPT, fraction by weight) with TiO_2 ($> 100\%$) are displayed in Fig. 1. The results obtained show that on calcination the initial potassium polytitanate crystallizes into a structure consisting of layered potassium tetratitanate $\text{K}_2\text{Ti}_4\text{O}_9$ particles, and adding additional TiO_2 in amounts 50 – 60% results in a structure consisting of fibrous potassium hexatitanate $\text{K}_2\text{Ti}_6\text{O}_{13}$ crystals as well as titanium oxide (anatase and/or rutile) crystals. In addition, the rutile fraction increases with increasing TiO_2 content.

The structure of the ceramic obtained is displayed in Fig. 2. It is shown that the structure of the ceramic formed by close-packed fibrous $\text{K}_2\text{Ti}_6\text{O}_{13}$ crystals becomes denser as the TiO_2 content increases. The titanium oxide crystals in the

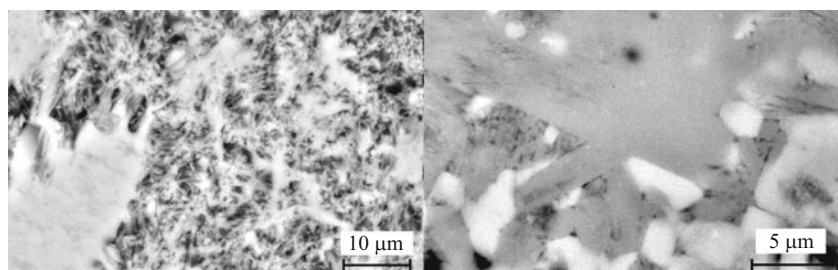


Fig. 2. The electronic photographs of the ceramic structure obtained on the basis of potassium polytitanate with added TiO_2 powder (fraction by weight > 100%) 30% (left-hand side) and 60% (right-hand side).

TABLE 1. Properties of Ceramic Materials Obtained by Sintering Green Parts Based on Mixtures (content by weight) of Potassium Polytitanate (PPT) and Titanium Oxide Powders

Raw material	Ceramic properties				
	Density, g/cm ³	Strength in compression, MPa	Microhardness, MPa	Heat-resistance, °C*	Friction coefficient
PPT (TiO ₂ /K ₂ O = 4.2)	2.78 ± 0.04	205	450 ± 31	1000	0.17 ± 0.01
PPT + 50% TiO ₂ (TiO ₂ /K ₂ O = 6.9)	3.07 ± 0.02	617 ± 21	510 ± 10	1300	0.19 ± 0.02
PPT + 60% TiO ₂ (TiO ₂ /K ₂ O = 7.4)	3.15 ± 0.02	695 ± 33	570 ± 23	1300	0.21 ± 0.02

* 20 temperature change (20°C — test temperature).

composite structure obtained play the role of a stabilizing additive, impeding unbounded growth of the potassium hexatitanate crystals and loosening the structure of the ceramic obtained.

The properties of the ceramic samples obtained with different ratio TiO₂/K₂O are presented in Table 1. The results of the measurements show that increasing the titanium oxide content in the raw mixture increases the apparent density of the ceramic and results in considerable growth of its mechanical strength, microhardness and resistance to thermal shock.

It is shown in [6] that the formation of ceramic structure from interwoven K₂Ti₆O₁₃ fibers results in very high crack resistance and resistance to thermal shock (1100°C). The presence of crystalline particles of titanium oxide in a ceramic based on mixtures of PPT and TiO₂ stabilizes this type of structure and increases the crack resistance and heat-resistance of the ceramic obtained to 1300°C (up to 20 temperature changes: 20 – 1300°C).

In summary, high-strength ceramic with very high resistance to thermal shock and low friction coefficient was obtained on the basis of potassium polytitanate powder and titanium oxide micropowders with relatively low pressing pressures on green compacts. Since potassium hexatitanate has a high reflection coefficient for thermal radiation (97% with thickness 3 mm [7]) and low wettability for melts of aluminum and its alloys [2, 3], ceramics of this type can be used in

different fields of engineering, specifically, to fabricate parts of friction units operating at high temperatures as well as in the presence of large temperature jumps (hundreds of degrees).

REFERENCES

1. Y. Hasegawa, H. Tanaka, and Y. Fujiki, "Some properties of single crystals of potassium hexatitanate," *J. Ceram. Soc. Jpn.*, **91**(12), 565 – 566 (1983).
2. T. Mitsunashi, H. Tanaka, and Y. Fujiki, "Thermal properties of sintered potassium hexatitanate," *J. Ceram. Soc. Jpn.*, **90**(11), 676 – 678 (1982).
3. H. Tanaka, N. Ohta, and Y. Fujiki, "Strength of sintered potassium hexatitanate," *J. Ceram. Soc. Jpn.*, **89**(5), 275 – 277 (1981).
4. J. I. Escalante-Garcia, T. Sanchez-Monjaras, and C. A. Gutierrez-Chavarria, "Synthesis of potassium polytitanate precursors by treatment of TiO₂ with molten mixtures of KNO₃ and KOH," *J. Eur. Ceram. Soc.*, No. 12, 3541 – 3546 (2004).
5. T. Sanchez-Monjaras, A. V. Gorokhovskiy, and J. I. Escalante-Garcia, "Molten salt synthesis and characterization of polytitanate ceramic precursors with varied TiO₂/K₂O molar ratio," *J. Am. Ceram. Soc.*, **91**(9), 3058 – 3065 (2008).
6. A. V. Gorokhovskiy, T. Sanchez-Monjaras, J. I. Escalante-Garcia, et al., "Influence of compaction conditions on the structure and mechanical properties of potassium titanate based ceramics," *Techn. Phys. Lett.*, **36**(1), 37 – 39 (2010).
7. H. C. Culledge, "Fibrous potassium titanate. A new high temperature insulating material," *Ind. Eng. Chem.*, **52**(2), 117 (1960).